Procedures for Sampling and Analyzing
Mainstream and Tributary Coordinated Split Samples

In June 1999, the Analytical Methods and Quality Assurance Workgroup (AMQAW) modified the design of the mainstem and tributary coordinated split sample program to provide a better assessment of inter-laboratory data comparability. Instead of using results from three replicate samples analyzed on the same day to estimate single laboratory variability, four samples are analyzed on two different days to include day-to-day variations in the calibration, temperature, humidity, holding time, etc. This allows a comparison of the variability among laboratories to the day-to-day variability within laboratories, ensuring that we are not expecting inter-laboratory variability to be better than the variability of single laboratory on different days.

The following parameters are analyzed for the split sample comparisons:

Total Dissolved Nitrogen (TDN)	Total Dissolved Phosphorus (TDP)
Particulate Nitrogen (PN)*	Phosphate (PO_4)
Nitrate + Nitrite (NO_{23})	Particulate Phosphorus (PP)*
Nitrite (NO_2)	Particulate Carbon (PC)*
Ammonia (NH_4)	Total Suspended Solids (TSS)
Chlorophyll *a*	Volatile Suspended Solids (VSS)
Pheophytin	Silica (Si)

* Two laboratories calculate particulate fractions by subtracting the dissolved fraction from total (unfiltered) result.

Mainstem Split Sample Collection Procedure

Every three months Department of Natural Resources staff collect split samples from the surface layer of mainstem station CB4.4. Water is collected with a submersible pump into a Nalgene 30 gallon carboy. One person continuously stirs the sample with a paint stirrer turned by an electric drill, and a second person dispenses one-gallon subsamples from the bottom spigot into pre-rinsed and labeled containers. Replicates are collected in the following sequence so that bias among subsamples can be checked:

Replicates A1, B1, C1, D1, E1, F1, then
Replicates A2, B2, C2, D2, E2, F2, then
Replicates A3, B3, C3, D3, E3, F3, then
Replicates A4, B4, C4, D4, E4, F4, then
Replicates A5, B5, C5, D5, E5, and F5.

Replicates are immediately placed into ice chests and transported to the laboratories at 4°C. The replicates are grouped as follows:

"A" Replicates (A1 - A5):	Maryland Department of Health and Mental Hygiene
"B" Replicates (B1 - B5):	Old Dominion University Water Quality Laboratory
"C" Replicates (C1 - C5):	University of Maryland Chesapeake Biological Laboratory
"D" Replicates (D1- D5):	Virginia Division of Consolidated Laboratory Services
"E" Replicates (E1 - E2):	Delaware State Environmental Laboratory (chlorophyll)
"E" Replicates (E3 - E5):	Academy of Natural Sciences Estuarine Research Center (chlorophyll)
"F" Replicates (F1 - F5):	Virginia Division of Consolidated Laboratory Services

Split Sample Analysis Procedure

1. Filter all 4 replicate samples before 8:00 a.m. the day after collection. Prepare and store the split samples exactly the same as routine samples. If two replicates are analyzed the day they are received, freeze the other two.

2. Analyze two of four replicate samples on one day and the remaining two replicates on a different day, within parameter holding times. If a holding time is exceeded, state this on the data report.

3. For dissolved parameters, spike one of the two replicates on each analysis day. Also, analyze a standard reference material on each analysis day. If there is sufficient sample volume, analyze a lab duplicate on each day also.

5. Report results for the following in the electronic format provided by Dave Jasinski:

Day 1	Day 2
Rep 1	Rep 3
Rep 2	Rep 4
Spike of Rep 1 or Rep 2	Spike of Rep 3 or Rep 4
Standard Reference Material	Standard Reference Material
Lab Duplicate of Rep 1 or Rep 2	Lab Duplicate of Rep 3 or Rep 4